



## Characteristics of the low temperature SCR of NO<sub>x</sub> with NH<sub>3</sub> over TiO<sub>2</sub>

Md. Azhar Uddin\*, Koichiro Shimizu, Koji Ishibe, Eiji Sasaoka

Department of Environmental Chemistry and Materials, Okayama University, 3-1-1 Tsushima-naka, Okayama 700-8530, Japan

### ARTICLE INFO

#### Article history:

Received 18 February 2009

Received in revised form 29 May 2009

Accepted 2 June 2009

Available online 10 June 2009

#### Keywords:

Low temperature SCR

NO<sub>x</sub>

TiO<sub>2</sub>

Activated carbon

SiO<sub>2</sub>

### ABSTRACT

Low temperature selective catalytic reduction (LT-SCR) of NO + NO<sub>2</sub> mixture with NH<sub>3</sub> was investigated over TiO<sub>2</sub>, SiO<sub>2</sub> and activated carbon in a conventional flow type fixed-bed reactor at 100 °C under atmospheric pressure. The effects of gas composition such as presence of SO<sub>2</sub> and NH<sub>3</sub> and the ratio of NO<sub>2</sub>/NO in the feed-stream on the LT-SCR have been studied. The presence of SO<sub>2</sub> and O<sub>2</sub> was essential for the selective removal of NO with NH<sub>3</sub> over TiO<sub>2</sub>. The presence of SO<sub>2</sub> contributed to the oxidation of NO to NO<sub>2</sub> over TiO<sub>2</sub>. If NO<sub>2</sub> existed with NO in the reaction system, the presence of SO<sub>2</sub> was not necessary for the removal of NO over TiO<sub>2</sub>. The following two reactions were suggested to occur over TiO<sub>2</sub>: NO + NO<sub>2</sub> + 2NH<sub>3</sub> → 2N<sub>2</sub> + 3H<sub>2</sub>O (1) and 2NO<sub>2</sub> + 2NH<sub>3</sub> → N<sub>2</sub> + NH<sub>4</sub>NO<sub>3</sub> + H<sub>2</sub>O (2). The reaction (2) occurred on all three catalysts, however the reaction (1) did not proceed significantly over SiO<sub>2</sub>.

© 2009 Elsevier B.V. All rights reserved.

### 1. Introduction

NO is one of the main atmospheric pollutants that can cause acid rain, and photochemical smog. The main sources of NO are the flue gases of fossil fuel combustion in power generation and automobiles mobile exhaust gases. The removal of NO from the flue gases and the emission of automobiles has been one of the main topics in atmospheric pollution control technologies. Among all the processes for the removal of NO, the most ideal process should be the direct decomposition of NO to N<sub>2</sub> and O<sub>2</sub>. However, the dissociation of NO requires very high temperature and no effective catalyst has been found for this reaction so far. A well-known achievable process, which had been commercialized, is selective catalytic reduction (SCR) of NO with NH<sub>3</sub>. The effective catalysts applied in SCR are V<sub>2</sub>O<sub>5</sub> with TiO<sub>2</sub> as a support material and WO<sub>3</sub> and MoO<sub>3</sub> as catalytic additives [1–4]. The disadvantage of the SCR of NO<sub>x</sub> with NH<sub>3</sub> over V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub>-based catalysts is that these catalysts are not effective below 250 °C. The outlet temperatures of flue gases containing NO<sub>x</sub> generated from electric power plants, shaft furnaces, and waste incinerators are usually lower than 150 °C. Therefore, it is necessary to develop a low temperature SCR process. An effective low temperature SCR process would permit NO<sub>x</sub> removal (DeNO<sub>x</sub>) unit to be installed downstream of the air preheater and electrostatic precipitators (ESP) for dust removal in some practical processes so that the attack by the NH<sub>3</sub> leaked from DeNO<sub>x</sub> unit on the equipment of the preheater and ESP could be avoided. The leaked NH<sub>3</sub> can be absorbed by the desulfurization process.

In recent years, considerable research efforts have been devoted to the development of low temperature SCR (LT-SCR) of NO with NH<sub>3</sub>. The most widely studied catalysts include active carbon fibers [5,6] metal oxides [7–9] and carbon fiber-supported metal oxides [10–13]. Most of the LT-SCR of NO reactions was studied at well above 100 °C.

The selective reduction of equimolar amounts of NO and NO<sub>x</sub> occurs at lower temperatures and with much faster rate than the reduction of NO according to the following reaction stoichiometry: NH<sub>3</sub> + NO + NO<sub>2</sub> → 2N<sub>2</sub> + 3H<sub>2</sub>O. This reaction was designated as “fast-SCR” by Koebel et al. [14,15]. The enhanced rate of this reaction has been long known and it is considered as one of the effective method for automotive NO<sub>x</sub> reduction [16,17]. Generally, NO<sub>x</sub> in diesel exhaust gas is mainly consists of NO, so a strong oxidation catalyst is necessary at the upstream of the SCR catalyst in order to increase the fraction of NO<sub>2</sub> in the exhaust. Pt-based catalysts are known to be very active for NO oxidation [18]. At low temperatures (<150 °C) NO<sub>2</sub> can react with NH<sub>3</sub> with the formation of ammonium nitrate according to the following reaction: 2NH<sub>3</sub> + 2NO<sub>2</sub> → NH<sub>4</sub>NO<sub>3</sub> + N<sub>2</sub> + H<sub>2</sub>O. The detail of this reaction is given in the literature [14]. This reaction may be considered as a selective DeNO<sub>x</sub> reaction since 50% of the NO<sub>2</sub> is reduced to N<sub>2</sub>. However, periodic removal of the ammonium nitrate salt from the catalyst surface by washing with H<sub>2</sub>O is needed for regeneration of the catalyst.

Previously we have reported that TiO<sub>2</sub>, ZrO<sub>2</sub>, and Al<sub>2</sub>O<sub>3</sub> catalyzed the LT-SCR of NO with NH<sub>3</sub> at 90 °C and the addition of Cl<sup>-</sup> and Br<sup>-</sup> ions to these catalysts enhanced the catalytic activities [19]. The main results obtained in these studies were that the SCR reaction was interrupted (ceased to occur) when SO<sub>2</sub> was absent from the feed gas indicating that SO<sub>2</sub> participated in the reduction process of

\* Corresponding author. Tel.: +81 86 251 8897 fax: +81 86 251 8897.  
E-mail address: [alazhar@cc.okayama-u.ac.jp](mailto:alazhar@cc.okayama-u.ac.jp) (Md.A. Uddin).

NO at low temperature. The mechanism of low temperature reduction of NO to N<sub>2</sub> was proposed to occur through an intermediate of NH<sub>4</sub>-NO<sub>2</sub>, which can be decomposed into N<sub>2</sub> and H<sub>2</sub>O below 100 °C. The activities of these three catalysts decayed with reaction time as a result of the accumulation of ammonium sulfate and nitrate salts plugging pores of the catalysts. However, the deactivated catalysts could be easily regenerated by washing with water. Although the SO<sub>2</sub> effects on the low temperature SCR DeNO<sub>x</sub> reaction have already been reported in our previous study for TiO<sub>2</sub>, ZrO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> catalysts, however the effect of NO and NO<sub>2</sub> ratio and the presence of H<sub>2</sub>O in the feed gas have not been studied yet.

In this work, the behavior the low temperature SCR of NO + NO<sub>2</sub> mixture with NH<sub>3</sub> over TiO<sub>2</sub>, SiO<sub>2</sub> and an activated carbon were studied. Particularly, the effects of NO<sub>2</sub>/NO ratio in the inlet gases on the LT-SCR of NO<sub>x</sub> were investigated in details.

## 2. Experimental

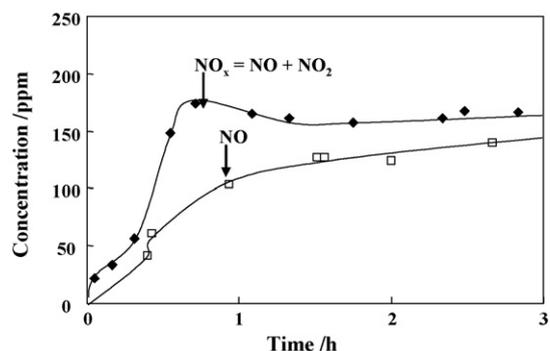
### 2.1. Materials

TiO<sub>2</sub> and SiO<sub>2</sub> and activated carbon were commercial samples (TiO<sub>2</sub> from, Sakai Chemicals Co.; SiO<sub>2</sub> from Mizusawa Chem. Ind. Co.; activated carbon from Wako Pure Chemical Co. Ltd.). TiO<sub>2</sub> and SiO<sub>2</sub> were calcined in air for at 500 °C for 1 h, and activated carbon (AC) was calcined in the N<sub>2</sub> flow at 500 °C for 1 h. The calcined samples were crushed and sieved to granules of 1.0 mm. The specific surface area of the TiO<sub>2</sub>, SiO<sub>2</sub> and AC was 86, 570 and 1200 m<sup>2</sup>/g, respectively and the bulk density of the samples (average grain size: 1.0 mm) was 0.82, 0.75 and 0.38 g/cm<sup>3</sup>, respectively.

### 2.2. Apparatus and procedure

The SCR reaction was carried out using a flow type fixed-bed tubular reactor system at 90–100 °C under atmospheric pressure. In a typical SCR experiment, 1 ml of catalyst was placed in the reactor made of a quartz tube of 1.5 cm i.d. and then catalyst bed was heated in N<sub>2</sub> flow to the desired reaction temperature with an electrical furnace equipped with an electronic temperature controller. The SCR reaction commenced when a mixture of NO (250 ppm), SO<sub>2</sub> (800 ppm), NH<sub>3</sub> (500 ppm), O<sub>2</sub> (5%), H<sub>2</sub>O (10%), CO<sub>2</sub> (14%), and N<sub>2</sub> balance was fed into the reactor at 200 cm<sup>3</sup> (STP)/min. This reaction conditions will be designated as standard system in this paper hereafter. The effect of feed gas composition was studied by changing the concentration of the corresponding components keeping the concentration of other gases constant except for N<sub>2</sub> which was used as a balance gas. The effect of NO<sub>2</sub>/NO in the feed was investigated by varying the NO<sub>2</sub>/NO<sub>x</sub> (NO<sub>x</sub> = NO + NO<sub>2</sub>) from 0 to 1, but keeping the total concentration of NO<sub>x</sub> at 250 ppm in the feed. The inlet and outlet concentration of NO and NO<sub>2</sub> was measured using a chemiluminescent NO analyzer (Yanako Co., Model ES-7) after NO<sub>2</sub> was converted to NO using a solution containing KI and H<sub>2</sub>SO<sub>4</sub> ( $2\text{K}^+\text{I}^- + \text{NO}_2 + \text{H}_2\text{O} \rightarrow \text{NO} + 2\text{K}^+\text{OH}^- + \text{I}_2$ ). Thus, when the effluent containing NO<sub>x</sub> is passed through the KI + H<sub>2</sub>SO<sub>4</sub> trap, NO analyzer gives the value for NO<sub>x</sub> concentration and when the stream is injected directly to NO analyzer it gives the concentration of NO only in the effluent. Therefore the difference between the NO<sub>x</sub> and NO concentration is the NO<sub>2</sub> concentration. The concentration of N<sub>2</sub> was analyzed using a GC (Yanako G3800) equipped with a thermal conductivity detector with molecular sieve 5A column. Ammonium nitrate, which was accumulated over the catalysts during the experiment, was detected with an ion chromatograph after dissolution in H<sub>2</sub>O.

In this paper, the results of NO<sub>x</sub> analyses are presented mainly as the concentration of NO and NO<sub>x</sub> (NO<sub>x</sub> = NO + NO<sub>2</sub>) at the inlet and outlet of the reactor. Generally, conversion of NO is used to



**Fig. 1.** Outlet concentration of NO<sub>x</sub> and NO for low temperature SCR of NO over TiO<sub>2</sub> catalyst. Inlet gas: NO (250 ppm), NH<sub>3</sub> (500 ppm), SO<sub>2</sub> (800 ppm), O<sub>2</sub> (5%), CO<sub>2</sub> (14%), H<sub>2</sub>O (10%), N<sub>2</sub> (balance), SV: 12,000 h<sup>-1</sup>; reaction temperature: 100 °C.

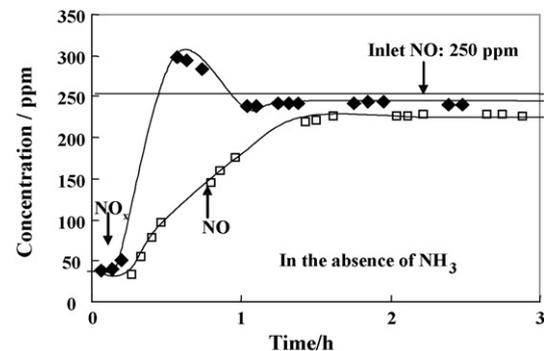
evaluate the catalytic activity for standard SCR process. In this work we investigated mainly the effect of NO<sub>2</sub>/NO ratio in the feed on the conversion of both NO and NO<sub>2</sub> during low temperature SCR and we presented our results with NO and NO<sub>x</sub> concentration which is more informative than the NO or NO<sub>x</sub> conversion data.

## 3. Results and discussion

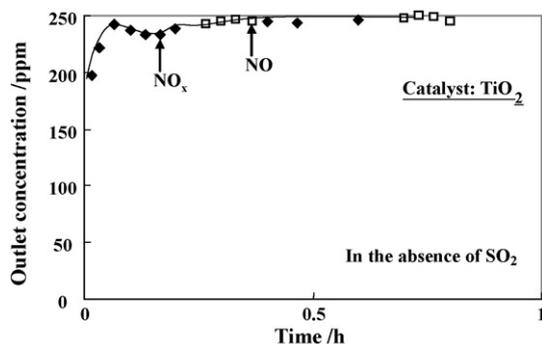
### 3.1. Effect of the presence of NH<sub>3</sub> and SO<sub>2</sub> on the removal of NO over TiO<sub>2</sub>

The effects of the presence of NH<sub>3</sub> and SO<sub>2</sub> on the low temperature SCR of NO were examined at 100 °C before studying the effect of NO<sub>2</sub>/NO ratio on SCR. Fig. 1 shows the outlet concentrations of NO and NO<sub>x</sub> (NO + NO<sub>2</sub>) as a function of time on stream. The concentration of NO at the reactor outlet increased with the time on stream at the initial stage and then became almost steady in the later stages. The initial low decrease in NO concentration is due to the adsorption of NO as adsorbed NO<sub>x</sub> species on the TiO<sub>2</sub> surface and steady state SCR of NO was achieved after about 1.5 h time on stream. It is also evident from Fig. 1 that a small amount of NO<sub>2</sub> was formed in the standard system and the NO<sub>2</sub> formation reached a steady state value through a maximum at around 0.5 h time on stream. This result suggested that the oxidation of NO occurred over the TiO<sub>2</sub> catalyst during the SCR. In our previous paper, we presented a mechanism that included the oxidation step as an elemental reaction [9].

In order to elucidate the effects of the presence of NH<sub>3</sub> on the oxidation of NO, the reaction was carried out in the absence of NH<sub>3</sub>. The NO<sub>2</sub> formation and/or desorption was accelerated in the absence of NH<sub>3</sub> as shown in Fig. 2. The overshoot in the NO<sub>x</sub> concentration



**Fig. 2.** Outlet concentration of NO<sub>x</sub> and NO in the absence of NH<sub>3</sub> over TiO<sub>2</sub> catalyst. Inlet gas: NO (250 ppm), NH<sub>3</sub> (0 ppm), SO<sub>2</sub> (800 ppm), O<sub>2</sub> (5%), CO<sub>2</sub> (14%), H<sub>2</sub>O (10%), N<sub>2</sub> (balance), SV: 12,000 h<sup>-1</sup>; reaction temperature: 100 °C.



**Fig. 3.** Outlet concentration of  $\text{NO}_x$  and  $\text{NO}$  in the absence of  $\text{SO}_2$  over  $\text{TiO}_2$  catalyst. Inlet gas:  $\text{NO}$  (250 ppm),  $\text{NH}_3$  (500 ppm),  $\text{SO}_2$  (0 ppm),  $\text{O}_2$  (5%),  $\text{CO}_2$  (14%),  $\text{H}_2\text{O}$  (10%),  $\text{N}_2$  (balance), SV:  $12,000 \text{ h}^{-1}$ ; reaction temperature:  $100^\circ\text{C}$ .

was induced by  $\text{NO}_2$  desorption, because the adsorbed  $\text{NO}_2$  was desorbed by the adsorption of  $\text{SO}_2$  as  $\text{SO}_3$  which is more strongly adsorbed than  $\text{NO}_2$ .

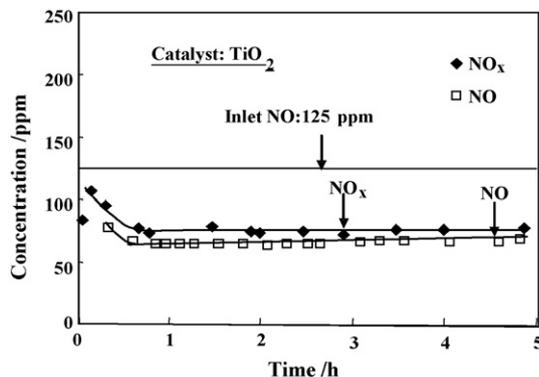
The results of the effect of  $\text{SO}_2$  on the SCR of  $\text{NO}$  with  $\text{NH}_3$  are shown in Fig. 3. We have previously reported that SCR of  $\text{NO}$  with  $\text{NH}_3$  did not occur in the absence of  $\text{SO}_2$  [9]. It is also evident in Fig. 3 that the outlet concentration of  $\text{NO}$  remained same as the inlet concentration i.e. no reaction occurred in the absence of  $\text{SO}_2$ . Moreover,  $\text{NO}_2$  formation was not observed in the absence of  $\text{SO}_2$  (data is not shown). From these results, it was confirmed that  $\text{SO}_2$  contributed to the  $\text{NO}$  oxidation and it was indispensable for the  $\text{NH}_3$ -SCR of  $\text{NO}$  at the low temperatures.

### 3.2. Effect of the presence of $\text{NO}_2$ on the $\text{NH}_3$ -SCR over $\text{TiO}_2$

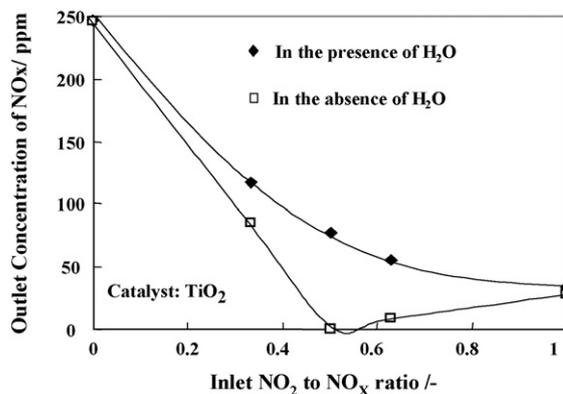
In order to confirm the hypothesis that the oxidation of  $\text{NO}$  to  $\text{NO}_2$  is an essential step in the LT-SCR of  $\text{NO}$ , the reaction was carried out in the absence of  $\text{SO}_2$ , but in the presence of  $\text{NO}_2$  with  $\text{NO}$  ( $\text{NO}$ : 125 ppm and  $\text{NO}_2$ : 125 ppm). As shown in Fig. 4, a large quantity of  $\text{NO}_x$  was removed even in the absence of  $\text{SO}_2$ : about 75% of inlet  $\text{NO}_x$  was disappeared, however about half of the  $\text{NO}$  remained unchanged. From this result, it might be concluded that in the presence of both  $\text{NO}$  and  $\text{NO}_2$ , the presence of  $\text{SO}_2$  is not essential for SCR. That is, the oxidation of  $\text{NO}$  to  $\text{NO}_2$  is indispensable step in the LT-SCR of  $\text{NO}$ .

### 3.3. Effect of the inlet $\text{NO}_2$ to $\text{NO}_x$ ratio on removal of $\text{NO}_x$ over $\text{TiO}_2$

As it was evident from Fig. 4 that oxidation of  $\text{NO}$  to  $\text{NO}_2$  is a necessary step for the LT-SCR of  $\text{NO}_x$ , it is of great interest to investigate

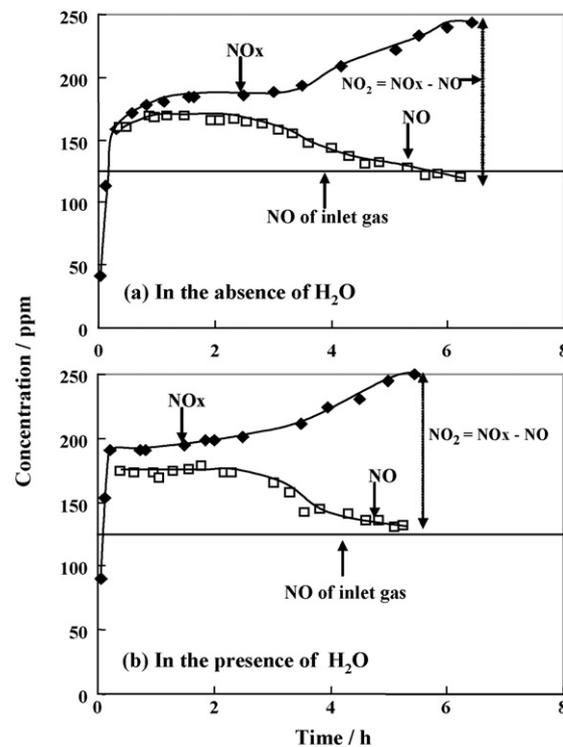


**Fig. 4.** Outlet concentration of  $\text{NO}_x$  and  $\text{NO}$  in the presence of  $\text{NO}_2$  and absence of  $\text{SO}_2$ . Inlet gas:  $\text{NO}$  (125 ppm),  $\text{NO}_2$  (125 ppm),  $\text{NH}_3$  (500 ppm),  $\text{SO}_2$  (0 ppm),  $\text{O}_2$  (5%),  $\text{CO}_2$  (14%),  $\text{H}_2\text{O}$  (10%),  $\text{N}_2$  (balance), SV:  $12,000 \text{ h}^{-1}$ ; reaction temperature:  $100^\circ\text{C}$ .



**Fig. 5.** Effect of inlet  $\text{NO}_2/\text{NO}_x$  ratio and water vapor on the low temperature SCR of  $\text{NO}$  over  $\text{TiO}_2$ . Inlet gas:  $\text{NO}_x$  ( $\text{NO} + \text{NO}_2 = 250 \text{ ppm}$ ),  $\text{NH}_3$  (500 ppm),  $\text{SO}_2$  (0 ppm),  $\text{O}_2$  (5%),  $\text{CO}_2$  (14%),  $\text{H}_2\text{O}$  (0% or 10%),  $\text{N}_2$  (balance), SV:  $12,000 \text{ h}^{-1}$ ; reaction temperature:  $100^\circ\text{C}$ .

the effect of ratio of  $\text{NO}_2$  to  $\text{NO}_x$  on SCR of  $\text{NO}_x$ . The effect ratio of  $\text{NO}_2$  to  $\text{NO}_x$  on the removal of  $\text{NO}_x$  was examined in the absence of  $\text{SO}_2$  over  $\text{TiO}_2$  at  $100^\circ\text{C}$ . In Fig. 5, the outlet concentration of  $\text{NO}_x$  was plotted against the inlet ratio of  $\text{NO}_2/\text{NO}_x$ . In the absence of  $\text{H}_2\text{O}$ , the outlet concentration of  $\text{NO}_x$  was the lowest at the  $\text{NO}/\text{NO}_x$  ratio of 0.5 i.e. at  $\text{NO}/\text{NO}_2$  ratio of 1.0. In the presence of  $\text{H}_2\text{O}$ , the outlet concentration of  $\text{NO}_x$  monotonically decreased with the increase of  $\text{NO}_2/\text{NO}$  ratio. The reason for the differences in the dependency of outlet concentration of  $\text{NO}_x$  on  $\text{NO}_2/\text{NO}_x$  ratio in the absence and presence of  $\text{H}_2\text{O}$  can be explained as follows: in the presence of  $\text{H}_2\text{O}$ , the inlet mole ratio of  $\text{NO}_2/\text{NO}_x$  might have changed on the catalyst surface before the occurrence of SCR. In order to confirm the conversion of  $\text{NO}_2$  to  $\text{NO}$ , the reaction was examined in the absence of  $\text{SO}_2$  and  $\text{NH}_3$ . Fig. 6 shows the outlet concentration of  $\text{NO}$  and  $\text{NO}_x$



**Fig. 6.** Effect of water vapor on the conversion of  $\text{NO}_2$  to  $\text{NO}$  in the absence of  $\text{SO}_2$  and  $\text{NH}_3$  over  $\text{TiO}_2$ . Inlet gas:  $\text{NO}$  (125 ppm),  $\text{NO}_2$  (125 ppm),  $\text{NH}_3$  (0 ppm),  $\text{SO}_2$  (0 ppm),  $\text{O}_2$  (5%),  $\text{CO}_2$  (14%),  $\text{H}_2\text{O}$  (0% or 10%),  $\text{N}_2$  (balance), SV:  $12,000 \text{ h}^{-1}$ ; reaction temperature:  $100^\circ\text{C}$ .

**Table 1**  
Concentration of N<sub>2</sub> formed on TiO<sub>2</sub>.

| Inlet ratio: NO <sub>2</sub> /NO <sub>x</sub> | NO <sub>3</sub> <sup>-</sup> formed/NO <sub>x</sub> reacted | Inlet NO <sub>x</sub> (ppm) | N <sub>2</sub> formed (ppm) |
|---|---|-----------------------------|-----------------------------|
| 0.5 (without H <sub>2</sub> O)                | 4   | 250                         | 266                         |
| 1.0 (without H <sub>2</sub> O)                | 46  | 250                         | 98                          |

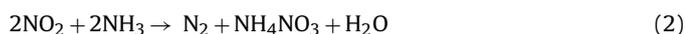
Reaction temperature: 100 °C; SV: 12,000 h<sup>-1</sup>, NO<sub>x</sub>: NO + NO<sub>2</sub>.

(NO + NO<sub>2</sub>) as a function of time on stream for the reaction of NO (125 ppm) and NO<sub>2</sub> (125 ppm) over TiO<sub>2</sub> in the absence of both NH<sub>3</sub> and SO<sub>2</sub>. It can be seen from Fig. 6(a) that in the presence of H<sub>2</sub>O, the outlet concentration of NO exceeded the inlet concentration of NO (125 ppm) for the first 2 h of stream. During this time, the concentration NO<sub>2</sub> (difference between the concentration of NO<sub>x</sub> and NO) decreased significantly. These results indicate that NO<sub>2</sub> was converted to NO on TiO<sub>2</sub> surface. However the outlet concentration of NO<sub>x</sub> (NO + NO<sub>2</sub>) was much lower than the inlet concentration of NO<sub>x</sub> (250 ppm) for the first 2 h. The differed amount in NO<sub>x</sub> concentration between the inlet and outlet streams can be attributed to the adsorption of NO<sub>x</sub> species on the TiO<sub>2</sub> surface. After about 2 h on stream, the outlet concentration of NO started to decrease and that of NO<sub>2</sub> started to increase until the catalytic surface became saturated with the adsorbed NO<sub>x</sub> species. As shown in Fig. 6(b), the NO<sub>x</sub> adsorption and NO oxidation were accelerated a little by the presence of H<sub>2</sub>O. From these experiments, we suggested that the NO<sub>2</sub>/NO<sub>x</sub> ratio on the surface of the catalyst was not the same as the inlet NO<sub>2</sub>/NO<sub>x</sub> ratio if the conversion of NO<sub>2</sub> to NO occurred much faster than the low temperature SCR.

In Figs. 4 and 5, we reported the decrease of NO<sub>x</sub> concentration due to the reactions that occurred over the TiO<sub>2</sub>, however it was not evident from these results whether the SCR of NO<sub>x</sub> to N<sub>2</sub> occurred on the TiO<sub>2</sub> surface. In order to elucidate the nature of LT-SCR of NO<sub>x</sub> over TiO<sub>2</sub> catalyst, we determined the formation of N<sub>2</sub> quantitatively with a gas chromatograph using He as a balance gas instead of N<sub>2</sub> in the feed. As shown in Table 1, almost all of the reduced NO<sub>x</sub> was converted to N<sub>2</sub> when the inlet NO<sub>2</sub>/NO<sub>x</sub> was controlled to 0.5 (i.e., with the equimolar amount of NO and NO<sub>2</sub> in the feed-stream) in the absence of H<sub>2</sub>O. From this result, it is evident that the following reaction, which has been reported to occur in the high temperature SCR [20] also occurred in this reaction system:



Furthermore, the amount of ammonium nitrate formed on the catalyst during the experiment was quantitatively analyzed with an ion chromatograph (Table 2). When the reaction was carried out at a NO<sub>2</sub>/NO<sub>x</sub> ratio of 1.0 (i.e., in the absence of NO), about half of the NO<sub>2</sub> reacted was converted to N<sub>2</sub> (shown in Table 1) and the other half was converted to ammonium nitrate (shown in Table 2). From this result, it is established that the following reaction occurred in this reaction system:

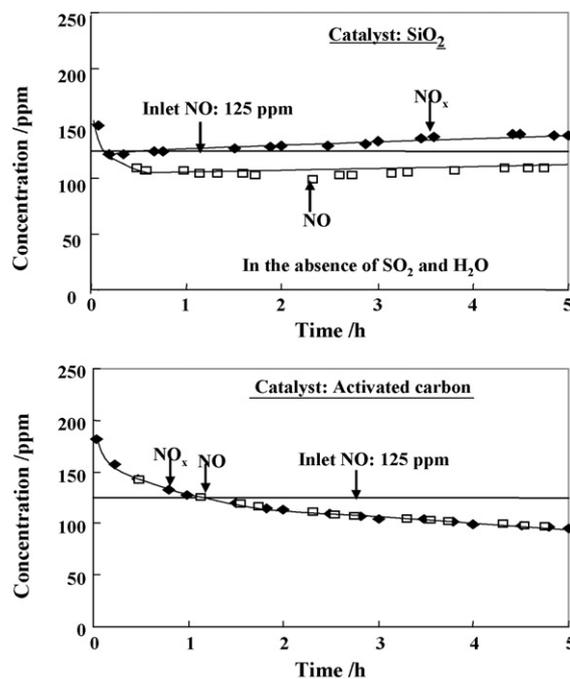


From the above results it can be suggested that both of the reactions (1) and (2) occur in the low temperature SCR of NO<sub>x</sub>. As shown in Table 2, in the presence of H<sub>2</sub>O at NO<sub>2</sub>/NO<sub>x</sub> = 0.5, a small amount of NO<sub>x</sub> was converted to NH<sub>4</sub>NO<sub>3</sub> and remained deposited

**Table 2**  
Amount of NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> ion formed on TiO<sub>2</sub> after 5 h on stream.

| Inlet ratio: NO <sub>2</sub> /NO <sub>x</sub> | NO <sub>x</sub> reacted (mol) | NO <sub>3</sub> <sup>-</sup> formed (mol) | NH <sub>4</sub> <sup>+</sup> formed (mol) | NO <sub>3</sub> <sup>-</sup> /NO <sub>x</sub> reacted (%) |
|---|-------------------------------|---|---|---|
| 0.5 (with H <sub>2</sub> O)                   | 4.6 × 10 <sup>-4</sup>        | 7.1 × 10 <sup>-5</sup>                    | 7.5 × 10 <sup>-5</sup>                    | 15  |
| 0.5 (without H <sub>2</sub> O)                | 6.7 × 10 <sup>-4</sup>        | 2.4 × 10 <sup>-5</sup>                    | 1.9 × 10 <sup>-4</sup>                    | 4   |
| 1.0 (with H <sub>2</sub> O)                   | 5.8 × 10 <sup>-4</sup>        | 2.9 × 10 <sup>-4</sup>                    | 2.0 × 10 <sup>-4</sup>                    | 49  |
| 1.0 (without H <sub>2</sub> O)                | 6.1 × 10 <sup>-4</sup>        | 2.8 × 10 <sup>-4</sup>                    | 3.9 × 10 <sup>-4</sup>                    | 46  |

Reaction temperature: 100 °C; SV: 12,000 h<sup>-1</sup>; NO<sub>x</sub>: NO + NO<sub>2</sub>.

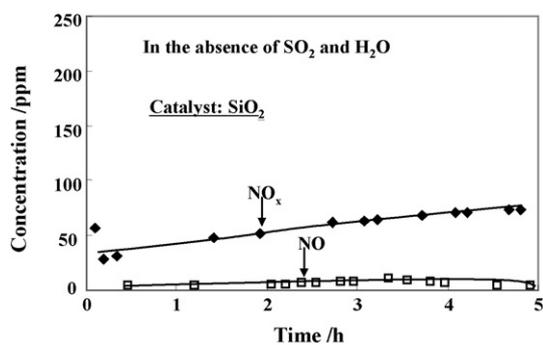


**Fig. 7.** Low temperature SCR of NO+NO<sub>2</sub> with ammonia over SiO<sub>2</sub> and activated carbon in the absence of SO<sub>2</sub> and H<sub>2</sub>O. Inlet gas: NO (125 ppm), NO<sub>2</sub> (125 ppm), NH<sub>3</sub> (500 ppm), SO<sub>2</sub> (0 ppm), O<sub>2</sub> (5%), CO<sub>2</sub> (14%), H<sub>2</sub>O (0%), N<sub>2</sub> (balance), SV: 12,000 h<sup>-1</sup>; reaction temperature: 100 °C.

on the used TiO<sub>2</sub> surface (NO<sub>3</sub><sup>-</sup>/NO<sub>x</sub> reacted = 15%). In the absence H<sub>2</sub>O, NO<sub>x</sub> was also converted to NH<sub>4</sub>NO<sub>3</sub>, however the amount of NH<sub>4</sub>NO<sub>3</sub> found on the used TiO<sub>2</sub> was 1/3 of that found in the presence of H<sub>2</sub>O. In the absence of H<sub>2</sub>O (at NO<sub>2</sub>/NO<sub>x</sub> = 0.5), the amount of NH<sub>4</sub><sup>+</sup> ion was higher than that of NO<sub>3</sub><sup>-</sup> ion. At present, the reason for this discrepancy is not known yet. With NO<sub>2</sub> to only in the feed as NO<sub>x</sub> species (i.e., NO<sub>2</sub>/NO<sub>x</sub> = 1.0), it is evident that half of the NO<sub>2</sub> reacted was converted to NH<sub>4</sub>NO<sub>3</sub> in the presence and absence of H<sub>2</sub>O. It is noteworthy that no N<sub>2</sub>O was formed in such low temperature on the catalysts used in this study. It is known that N<sub>2</sub>O can be formed as an undesired product from oxidation of NH<sub>3</sub> with O<sub>2</sub> over Pt–Rh catalyst at high temperature and high pressure.

### 3.4. Low temperature NH<sub>3</sub>-SCR over SiO<sub>2</sub> and activated carbon

As the reaction (1) and (2) occurred over the TiO<sub>2</sub> in the absence of SO<sub>2</sub>, it was thought that these reactions may also occur over other porous material in the NO–NO<sub>2</sub> stream. In order to confirm this idea, the activity of SiO<sub>2</sub> and the activated carbon for LT-SCR was examined in the NO–NO<sub>2</sub> system. Fig. 7 shows the outlet concentration of NO<sub>x</sub> during the SCR over SiO<sub>2</sub> and activated carbon for equimolar amount of NO and NO<sub>2</sub> in the feed and in the absence of SO<sub>2</sub> and H<sub>2</sub>O. For SiO<sub>2</sub>, the outlet concentration of NO decreased slightly from the inlet concentration and the outlet concentration of NO<sub>2</sub> (difference between the concentration of NO<sub>x</sub> and NO in Fig. 7) was very low. With activated carbon, initially the outlet concentration of NO increased slightly than the inlet NO concentration (up to



**Fig. 8.** Outlet concentration of  $\text{NO}_x$  and  $\text{NO}$  over  $\text{SiO}_2$  in the absence of  $\text{SO}_2$  and  $\text{H}_2\text{O}$ . Inlet gas:  $\text{NO}_2$  (250 ppm),  $\text{NH}_3$  (500 ppm),  $\text{SO}_2$  (0 ppm),  $\text{O}_2$  (5%),  $\text{CO}_2$  (14%),  $\text{H}_2\text{O}$  (0%),  $\text{N}_2$  (balance),  $\text{SV}$ :  $12,000 \text{ h}^{-1}$ ; reaction temperature:  $100^\circ\text{C}$ .

0.5 h on stream), however no  $\text{NO}_2$  was detected in the reactor outlet. These results indicate that mainly the reaction (2) occurred over  $\text{SiO}_2$  and activated carbon involving  $\text{NO}_2$ . The following reactions (3)–(6) are the elemental steps of reaction (2).



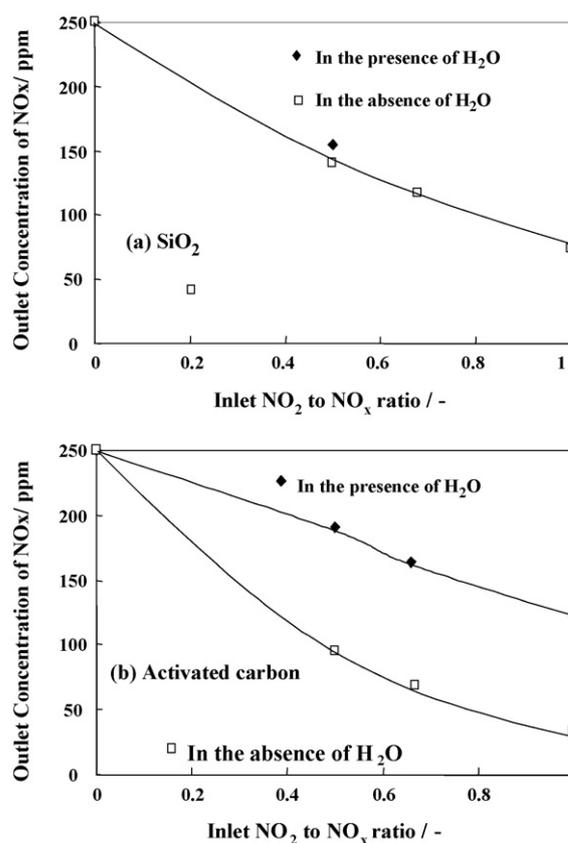
These reactions have been proposed as elemental steps of reaction (2), and some of these reactions are known to occur in the nitric acid production process.

The reaction mechanism of fast-SCR i.e. reaction (1) is not well understood yet. Sun et al. [21] proposed a mechanism for low temperature  $\text{NO}$  reduction with ammonia on Fe-ZSM-5 catalysts. They assume that  $\text{NO}$  and  $\text{NO}_2$  reacted with  $\text{H}_2\text{O}$  and  $\text{NH}_3$  to form ammonium nitrate which decomposed to  $\text{N}_2$ . We may suggest the following individual reaction steps for reaction (1):



The idea is that  $\text{N}_2\text{O}_3$ , formed from  $\text{NO}_2$  and  $\text{NO}$ , reacts with  $\text{H}_2\text{O}$  according to the reaction (8) forming  $\text{HNO}_2$ . Then  $\text{N}_2$  is produced via the formation and decomposition of ammonium nitrite according to reactions (5') and (6') as indicated by Koebel et al. [14]. Ammonium nitrite is known to be very unstable compounds decomposing at temperatures above  $60^\circ\text{C}$ .

We assumed that a catalyst which has some activity for the reaction (2) might also have some activity for the reaction (1). However,  $\text{SiO}_2$  and activated carbon have some activity only for the reaction (2) but no activity for reaction (1) was observed as shown in Fig. 7. From these results, it may be concluded that our assumptions are not correct. For the clarification of these two mechanisms, more detailed studies are needed. The activity of the  $\text{SiO}_2$  for reaction (2) was examined in the  $\text{NO}_2$  system in the absence of  $\text{SO}_2$  and  $\text{H}_2\text{O}$ . As shown in Fig. 8, the activity was slightly lower than that of  $\text{TiO}_2$  (shown in Fig. 5). This result indicates that the reaction (2) occurred catalytically on  $\text{SiO}_2$ . Therefore, it may be possible that the reaction (2) can be used as a step of  $\text{NH}_3$ -SCR at low temperature using porous catalysts such as  $\text{SiO}_2$ , if  $\text{NO}$  can be converted to  $\text{NO}_2$  over a separate (or different) catalyst in the first step.



**Fig. 9.** Effect of inlet  $\text{NO}_2/\text{NO}_x$  ratio and water vapor on the low temperature SCR over (a)  $\text{SiO}_2$  and (b) activated carbon. Inlet gas:  $\text{NO}_x$  ( $\text{NO} + \text{NO}_2 = 250 \text{ ppm}$ ),  $\text{NH}_3$  (500 ppm),  $\text{SO}_2$  (0 ppm),  $\text{O}_2$  (5%),  $\text{CO}_2$  (14%),  $\text{H}_2\text{O}$  (0% or 10%),  $\text{N}_2$  (balance),  $\text{SV}$ :  $12,000 \text{ h}^{-1}$ ; reaction temperature:  $100^\circ\text{C}$ .

### 3.5. Effect of the inlet $\text{NO}_2$ to $\text{NO}_x$ ratio on removal of $\text{NO}_x$ over $\text{SiO}_2$ and activated carbon

The effect of inlet  $\text{NO}_2$  to  $\text{NO}_x$  ratio and the presence of  $\text{H}_2\text{O}$  on the removal of  $\text{NO}_x$  were examined in the absence of  $\text{SO}_2$  over  $\text{SiO}_2$  and activated carbon at  $100^\circ\text{C}$ . In Fig. 9, the outlet concentration of  $\text{NO}_x$  was plotted against the inlet ratio of  $\text{NO}_2/\text{NO}_x$  for (a)  $\text{SiO}_2$  and (b) activated carbon. Unlike the case with  $\text{TiO}_2$  (Fig. 5), water vapor has no effect on the removal of  $\text{NO}_x$  over  $\text{SiO}_2$ . Moreover, the  $\text{NO}_x$  removal rate on  $\text{SiO}_2$  is much lower than that on  $\text{TiO}_2$ . As we mentioned earlier that reaction (1) is suppressed by the presence of  $\text{H}_2\text{O}$ , the above results indicate that reaction (1) did not occur on  $\text{SiO}_2$ . It is also worth mentioning that for  $\text{TiO}_2$ ,  $\text{H}_2\text{O}$  has no effect on the reaction (2). Accordingly, we can suggest that the reaction (2) which is not affected by the presence of  $\text{H}_2\text{O}$  occurred on  $\text{SiO}_2$ . On the other hand activated carbon showed different activity compared to  $\text{SiO}_2$  for this reaction system: in the absence of  $\text{H}_2\text{O}$ ,  $\text{NO}_x$  removal behavior was quite similar to that of  $\text{TiO}_2$  in the presence of  $\text{H}_2\text{O}$  (Fig. 5), i.e.  $\text{NO}_x$  removal rate increased smoothly with the increase of  $\text{NO}_2/\text{NO}_x$  inlet ratio (i.e. with the increase of  $\text{NO}_2$  concentration). In the presence of  $\text{H}_2\text{O}$ ,  $\text{NO}_x$  removal rate also increased with the increase of  $\text{NO}_2/\text{NO}_x$  inlet ratio linearly, however the extent of  $\text{NO}_x$  removal rate was much lower than in the absence of  $\text{H}_2\text{O}$ .

From the above results, no correlation between the specific surface area and the  $\text{deNO}_x$  activities of the catalysts was observed. Although the surface area of  $\text{TiO}_2$  is the smallest, it provides the highest catalytic activity for  $\text{NO}_x$  reduction. The surface characteristics of catalysts such as Brønsted acid/base sites in  $\text{TiO}_2$  catalysts can affect the  $\text{deNO}_x$  behavior of  $\text{TiO}_2$  catalysts. The conventional

high temperature SCR reaction is a redox process that occurs with a redox or Mars–van Krevelen-type mechanism on vanadium-based (containing TiO<sub>2</sub>) catalysts. Ammonia adsorbs on acid sites in two different strongly held species: (i) molecularly adsorbed ammonia, through a Lewis-type interaction and (ii) ammonia observed as ammonium ions, over Brønsted acidic–OH surface hydroxyl groups [22–24]. TiO<sub>2</sub> (anatase) surface has active centers of both Lewis and Brønsted types, with which ammonia interacts via coordination bonding or by the creation of ammonium-ion (NH<sub>4</sub><sup>+</sup>). It has been shown that NO is adsorbed on TiO<sub>2</sub> forming of a surface nitrosyl species, coordinated to Ti<sup>4+</sup> sites [25]. It is also known that presence of water molecule can increase the Brønsted acidity of TiO<sub>2</sub> or convert Lewis acid sites to Brønsted acid sites. On the other hand, it has also been reported for the study of influence of H<sub>2</sub>O on the acidity of TiO<sub>2</sub> using adsorption NH<sub>3</sub> as a basic probe molecule that the primary effect of H<sub>2</sub>O is displacement of strongly adsorbed basic probe molecules from Brønsted sites, rather than the conversion of Lewis sites to Brønsted sites [26]. In our present study we have not determined the amount of acid amount and acid sites of the catalysts by adsorption of any probe molecules. So, the effect of acid sites of the catalysts on the low temperature DeNO<sub>x</sub> activity of TiO<sub>2</sub> in the presence of water cannot be clarified at this stage.

#### 4. Conclusions

Low temperature SCR of NO + NO<sub>2</sub> mixture with NH<sub>3</sub> over TiO<sub>2</sub>, SiO<sub>2</sub> and activated carbon were studied using a conventional flow type packed-bed reactor at 100 °C under atmospheric pressure. The presence of SO<sub>2</sub>, and NH<sub>3</sub> was essential for the removal of NO over TiO<sub>2</sub>. SO<sub>2</sub> played a vital role in the oxidation of NO to NO<sub>2</sub> over TiO<sub>2</sub>. In the coexistence of NO and NO<sub>2</sub> in the reaction system, the presence of SO<sub>2</sub> is not essential for the SCR of NO over TiO<sub>2</sub>. The NO<sub>x</sub> removal activity was highest at the NO/NO<sub>2</sub> molar ratio of 1. It was clarified that the following two reactions occurred over TiO<sub>2</sub>: NO + NO<sub>2</sub> + 2NH<sub>3</sub> → 2N<sub>2</sub> + 3H<sub>2</sub>O (1) and

2NO<sub>2</sub> + 2NH<sub>3</sub> → N<sub>2</sub> + NH<sub>4</sub>NO<sub>3</sub> + H<sub>2</sub>O (2). The reaction (2) occurred on all three catalysts, however the reaction (1) did not proceed significantly over SiO<sub>2</sub>.

#### Acknowledgment

This work was supported by 21th COE program of Okayama University.

#### References

- [1] M. Takagi, T. Kawai, M. Soma, T. Onishi, K. Tamaru, *J. Catal.* 50 (1977) 441–446.
- [2] J.A. Odriozola, H. Heinemann, G.A. Somorjai, *J. Phys. Chem.* 95 (1991) 240.
- [3] J.P. Chen, R.T. Yang, *Appl. Catal. A* 80 (1992) 135–148.
- [4] J.W. Byrne, J.M. Chen, B.K. Sponello, *Catal. Today* 13 (1992) 33.
- [5] J. Muniz, G. Marban, A.B. Fuertes, *Appl. Catal. B* 23 (1999) 25–35.
- [6] J. Muniz, G. Marban, A.B. Fuertes, *Appl. Catal. B* 27 (2000) 27–36.
- [7] G. Qi, R.T. Yang, *J. Catal.* 217 (2003) 434–441.
- [8] R.Q. Long, R.T. Yang, R. Chang, *Chem. Commun.* (2002) 452–453.
- [9] F. Notoya, C. Su, E. Sasaoka, *Ind. Eng. Chem. Res.* 40 (2001) 3732–3739.
- [10] M. Yashikawa, A. Yasutake, I. Mochida, *Appl. Catal. A* 173 (1998) 239–245.
- [11] G. Marban, R. Antuna, A.B. Fuertes, *Appl. Catal. B* 41 (2003) 323–338.
- [12] Z. Huang, Z. Zhu, Z. Liu, Q. Liu, *J. Catal.* 214 (2003) 213–219.
- [13] Z. Zhu, Z. Liu, H. Miu, S. Liu, T. Hu, T. Liu, Y. Xie, *J. Catal.* 197 (2001) 6–16.
- [14] M. Koebel, M. Elsener, G. Madia, *Ind. Eng. Chem. Res.* 40 (2001) 52–59.
- [15] M. Koebel, G. Madia, M. Elsener, *Catal. Today* 73 (2002) 239–247.
- [16] A. Kato, S. Matsuda, F. Nakajima, H. Kuroda, T. Narita, *J. Phys. Chem.* 85 (1981) 4099–4102.
- [17] G. Tuenter, W. Leeuwen, L. Snejvangers, *Ind. Eng. Chem. Prod. Res. Dev.* 25 (1986) 633–636.
- [18] R. Marques, P. Darcy, P. Da Costa, H. Mellottee, J.-M. Trichard, G. Djega-Mariadassou, *J. Mol. Catal. A* 221 (2004) 127–136.
- [19] C. Su, F. Notoya, E. Sasaoka, *Ind. Eng. Chem. Res.* 42 (2003) 5770–5774.
- [20] S. Kasaoka, E. Sasaoka, M. Nagahiro, K. Kawakami, *Nippon Kagaku Kaishi* 1 (1979) 138–144.
- [21] Q. Sun, Z.-X. Gao, H.-Y. Chen, W.M.H. Sachtler, *J. Catal.* 201 (2001) 88–89.
- [22] M. Inomata, K. Mori, A. Miyamoto, T. Ui, Y. Murakami, *J. Phys. Chem.* 87 (1983) 754–761.
- [23] N.Y. Topsoe, *J. Catal.* 128 (1991) 499–511.
- [24] T.J. Dines, C.H. Rochester, A.M. Ward, *J. Chem. Soc. Faraday Trans.* 87 (1991) 1611–1617.
- [25] G. Ramis, G. Busca, F. Bregani, P. Forzatti, *Appl. Catal.* 64 (1990) 259–278.
- [26] A.P. Kulkarni, D.S. Muggli, *Appl. Catal. A: Gen.* 302 (2006) 274–282.